

The Soret and Dufour Effects in Statistical Dynamics

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Abstract

We set up a discrete space-time dynamical model of molecules with thermalised kinetic energy and repulsive cores, in an external potential. The model obeys the first and second laws of thermodynamics. The continuum limit, obtained using a MAPLE program, gives rise to coupled reaction-diffusion equations for the density and temperature fields. The system obeys Onsager symmetry and exhibits the Soret and Dufour effects.

Keywords: Soret, Dufour, reaction, diffusion, hard-core, dense gas.

1 Introduction

It was known from experiments in the Nineteenth Century that a liquid at uniform temperature, but with a gradient in its concentration, develops a non-uniform temperature (the Dufour effect); this was confirmed by Waldmann [27]. Thus Fourier's law [13] needs modification. A local version of the Thompson effect [26] was also found, in 1856, by Ludwig: if the density of a liquid is uniform, but the temperature is nonuniform, then there is a transport of matter. Thus, Fick's law [12] needs modification. The ratio of the molecular migration to the temperature gradient is called the Soret coefficient, after C. Soret, who studied the phenomenon in 1879-81 [19]. For gases, the Soret effect, under the name 'thermal diffusion', was obtained theoretically in 1911 by Enskog [11] using kinetic theory, and also by Chapman

in 1912 [5]. In Enskog's work, it showed up in the Lorentzian gas but not in the Maxwellian gas. It was first observed experimentally in gas mixtures by Chapman and Dootson [7].

Concerning Enskog's work, Hirschfelder et al. say "Each time we lower the level of description it is necessary to introduce a condition which restricts the possible states under consideration. In this case [Enskog's method] it is not clear how the restriction has been imposed" [14], p. 492. In the present paper we derive a model of a dense fluid using the methods of statistical dynamics [21], which is a systematic way to reduce the level of description. The possible states are restricted using information geometry in a well-defined way [15, 1]. In the present model, the essential part of the dynamics, the random hopping of molecules to neighbouring holes, is included, but there is no interparticle potential. The kinetic energy of the particles is fully thermalised, in the spirit of Smoluchowski [4]. We find that the model exhibits both the Dufour and the Soret effects, while obeying the first and second laws of thermodynamics. This success seems to contradict the statement of [6], p. 103: "No really satisfactory simple theory of this thermal diffusion can be given...The reason is that thermal diffusion is an interaction phenomenon. Similar remarks apply to the inverse 'diffusion thermo-effect' [the Dufour effect in gases]". Our theory, statistical dynamics, is not as simple as that using free paths referred to in this quotation, and it may be a matter of opinion whether it is 'really satisfactory'; however we do show that the effects follow from the assumptions that the state is in local thermal equilibrium, and that the hopping rate is proportional to the kinetic energy. These are kinematic assumptions, and do not require the solving of a model with an explicit interaction between the particles. The interaction enters only implicitly; its effect is replaced by the hopping term and the exclusion principle, followed by local thermalisation. So the last part of the quotation is not true.

In our model, the system is described by the particle density $\rho(x, t)$ and the temperature field $\Theta(x, t)$. The potential energy of a particle at x is $V(x)$, and the heat capacity is unity. Thus the density of heat is $\rho\Theta$. There is a maximum possible density, denoted ρ_m ; this corresponds to a hard core of diameter ℓ , where $\rho_m = \ell^{-\nu}$ in ν dimensions. The particle current j_c , and the heat current j_γ , are given in terms of ρ , Θ by

$$j_c = -\lambda(\Theta\nabla\rho + \rho(1 - \rho/\rho_m)\nabla(\Theta + V)) \quad (1)$$

$$j_\gamma = 2(\Theta j_c - \lambda\rho(1 - \rho/\rho_m)\Theta\nabla\Theta). \quad (2)$$

Here λ is the microscopic hopping rate. These relations in conjunction with

the conservation laws

$$\frac{\partial \rho}{\partial t} + \text{div } j_c = 0; \quad \frac{\partial(\rho\Theta)}{\partial t} + \text{div } j_\gamma = -j_c \cdot \nabla V \quad (3)$$

determine the dynamics. The heat current j_γ is not conserved, because of the heat source $-j_c \cdot \nabla V = j_c \cdot F$, where F is the force. Thus the work done by the field is entirely converted into heat; we call this the Smoluchowski point of view, though it is implicit in [9]. The current

$$j_e = j_\gamma + V j_c \quad (4)$$

of the energy density $\rho(\Theta + V)$ is conserved, as it obeys

$$\frac{\partial}{\partial t} \rho(\Theta + V) + \text{div } j_e = 0. \quad (5)$$

Thus the system obeys the first law of thermodynamics.

The particle current j_c carries with it, by convection, a heat flow of Θj_c . This already suggests that the Dufour effect is to be expected. The surprise here is that the Dufour effect is $2\Theta j_c$, double what is expected from this intuitive argument. We call the difference the ‘anomalous convection’. The Soret effect comes from the term $-\lambda\rho(1 - \rho/\rho_m)\nabla\Theta$ in j_c . This remains non-zero as $\rho_m \rightarrow \infty$, so the effect does not depend on the presence of a hard core. We see that in this limit, the Soret coefficient $j_c/(\rho\nabla\Theta)$ is λ . The fact that in eq. (5) the temperature is added to the external potential shows that the temperature gradient will cause a flow of particles; if they are charged, this will be interpreted as the thermo-electric effect.

The rest of the paper is organised as follows. In §2 we outline the model in discrete space and time. It is a version of the Boltzmann equation, with discrete energy rather than discrete velocity. It is thus closer to [16] than [17]. The collision operator is a bistochastic matrix T conserving energy and particle number (but no other quantities); it causes transitions (hopping) between particles and holes which are nearest neighbours. The discrete system is thermodynamically consistent in its own right, and thus forms the natural discretisation of the continuum equations of motion eq. (2). The state of the system at any time is described by giving the means of the ‘slow variables’, here taken to be the particle number, $n = 0$ or $n = 1$, and the kinetic energy, at each site. This information defines a unique grand canonical state at each site; the assumption that this is the state of the system after a small time-step is called *LTE*, the hypothesis of local thermodynamic equilibrium.

It means that the state is specified by giving the density and temperature fields, which define a point on our information manifold, \mathcal{M} . The dynamics of the state in one time-step is given by applying the map T , followed by projection of the resulting state back to \mathcal{M} .

In §3 the continuum limit of the dynamics is taken, with the help of MAPLE. The size of the lattice spacing ℓ and the time step dt are arranged to satisfy $dt = \ell^2$, known as the diffusion limit. This ensures that the limit exists; it gives the dynamics above.

In §4, we verify that the system can be put in Onsager form, though it is neither linear nor near equilibrium. Onsager symmetry is then seen to relate the Soret effect to the *anomalous* convection, which is thus the true dual or ‘inverse’ to the Soret effect.

In §5 we summarise the paper, and conclude that our simple model, without any momentum or angular momentum, and with unrealistic density of states, is able to exhibit the Soret effect and its dual without the pain of solving a model with interparticle interactions. There is no reason to expect that these qualitative conclusions would be altered by a more elaborate model. For example, we could add a direct transfer of kinetic energy between occupied sites; this adds further terms to the energy current, and increases the diagonal part of the Onsager matrix, without affecting the cross terms (the Soret and Dufour terms).

2 The Discrete Model with Hard Core

We start with a finite lattice $\Lambda \subseteq \ell\mathbf{Z}^\nu$, where ν is the dimension of space. A typical point of Λ will be denoted by x . At each site x there can be at most one molecule; this expresses the physical idea that the molecule has a repulsive core of diameter ℓ . We take a very simple model of the molecule; it has no spin or velocity, and its possible states are labelled by $k \in \{0, 1, 2, \dots\}$, denoting the kinetic energy $\mathcal{K} = k\epsilon$; here $\epsilon > 0$ represents a quantum of energy. This absence of velocity as a label for the point in phase space leads to a useful simplification of the mathematics compared with the discrete velocity Boltzmann equation [17]; we call it the Smoluchowski point of view. The sample space at x is thus

$$\Omega_x = \{\emptyset, 0, 1, 2, \dots\} = \{\emptyset\} \cup \mathbf{N}. \quad (6)$$

Here, $\omega_x = \emptyset \in \Omega_x$ means that the site x is empty, and $\omega_x = k_x \in \mathbf{N}$ means that the site x is occupied, and that its kinetic energy is $k_x\epsilon$. We can argue

that the fluctuation of the velocity of a real gas from its local mean value (the drift) is a fast variable, and is thermalised in one time-step. In this model, momentum is not accounted for; however, kinetic energy is.

The sample space, also known as the phase space, for the system is taken to be

$$\Omega = \prod_{x \in \Lambda} \Omega_x; \quad (7)$$

the motivation for choosing this is given in [22]. The product structure of Ω ensures that the particles are indistinguishable, since a configuration is given by a field $\{\omega_x\}_{x \in \Lambda}$. Thus the Gibbs paradox is avoided from the start, and there is no need to introduce symmetrising factors. In a classical stochastic description of such a system, an *observable* is a random variable, that is, a real function on Ω . The set of all bounded random variables form an algebra, denoted here by \mathcal{A} . At time $t \in \mathbf{N}$ the state of the system is described by a probability measure on Ω , which we denote by p ; in the theory of C^* -algebras, p is called a normal state on \mathcal{A} . The set of normal states is a convex set denoted by Σ .

A useful observable is the number of particles at x :

$$\mathcal{N}_x(\omega) = \begin{cases} 0 & \text{if } \omega_x = \emptyset, \\ 1 & \text{if } \omega_x \in \mathbf{N}. \end{cases} \quad (8)$$

The total number of particles is then the random variable

$$\mathcal{N}(\omega) = \sum_{\omega \in \Lambda} \mathcal{N}_x(\omega). \quad (9)$$

We introduce an external potential $V(x)$ for the particles. Contrary to [6], we shall not find it necessary to introduce an interaction between the particles in order to get the Soret and Dufour effects. The full treatment of a model with interaction leads to a much more complicated theory than the present one. The ‘mean field’ treatment of the interaction can be handled as in [2]; in this approximation, the interaction does contribute to the Soret effect, but is not the whole story.

The total energy is the random variable

$$\mathcal{E} = \mathcal{K} + \mathcal{V} \quad (10)$$

where

$$\mathcal{V}(\omega) = \sum_x V(x) \mathcal{N}_x(\omega); \quad \mathcal{K}(\omega) = \sum_x \epsilon k_x \mathcal{N}_x(\omega), \quad (11)$$

$\epsilon > 0$ being an energy unit, and

$$\omega = \{\omega_x\}_{x \in \Lambda}, \quad \omega_x = \emptyset \text{ or } k_x. \quad (12)$$

We are interested in states with finite mean energy

$$p \cdot \mathcal{E} := \sum_{\omega} p(\omega) \mathcal{E}(\omega) < \infty, \quad (13)$$

and finite partition function

$$Z = \sum_{\omega} e^{-\beta \mathcal{E}(\omega)} < \infty \quad \text{for all } \beta > 0; \quad (14)$$

this expresses thermodynamic stability.

The function \mathcal{E} divides Ω into disjoint energy shells:

$$\Omega_E = \{\omega \in \Omega : \mathcal{E}(\omega) = E\}, \quad \Omega = \bigsqcup_E \Omega_E.$$

Each Ω_E must be a finite set, because of eq. (14). Similarly we can write

$$\Omega_E = \bigsqcup_n \Omega_{E,n},$$

where

$$\Omega_{E,n} = \Omega_E \cap \Omega_n, \quad \Omega_n = \{\omega \in \Omega : \mathcal{N}(\omega) = n\}.$$

The next step in constructing the model is to give a bistochastic map T on Σ , representing one time-step of the linear part of the dynamics. This replaces the ‘collision term’ of the full Boltzmann equation. In place of the large number of collision invariants of the Boltzmann equation, we require just two conserved quantities, the energy and the particle number. Now, T is determined by linearity from its action on the point measures $\delta_{\omega, \omega'}$, and these can be identified with the points of Ω [20]. To conserve \mathcal{E} and \mathcal{N} , T must map each $\Omega_{E,n}$ to itself. When we give T , we are specifying the conditional probability of transition from ω to ω' . We do not attempt to find the most general bistochastic map, but limit ourselves to the case where

1. $T_{\omega, \omega'} = T_{\omega', \omega}$, the symmetric case.
2. $T_{\omega, \omega'} = 0$ if ω and ω' differ at points $x, x' \in \Lambda$ which are not nearest neighbours.

3. A transition occurs only by the movement of a particle; there is no direct transfer of kinetic energy between adjacent particles.

To conserve energy, any change in potential energy in a transition must be balanced by the opposite change in kinetic energy. Since the latter is an integral multiple of ϵ , we must suppose that all differences $V(x) - V(y)$, with $x, y \in \Lambda$, are integral multiples of ϵ . We shall work out the model in detail when $\nu = 1$, and Λ is an ‘interval’ of contiguous points in $\ell\mathbf{Z}$. Thus, for $x \in \Lambda$ with $x + \ell$ also in Λ , we can write

$$V(x + \ell) - V(x) = \epsilon w_x, \quad \text{with } w_x \in \mathbf{Z}. \quad (15)$$

Because of (2) and (3), above, the possible transitions involve the movement of a particle from x to a hole at $x + \ell$ or $x - \ell$, or *vice versa*. We shall choose x , and consider the case $w_x > 0$; other cases are treated similarly.

Suppose that there is a particle at x and a hole at $x + \ell$. In order for the transition $x \mapsto x + \ell$ to be possible, the kinetic energy of the particle at x must be at least ϵw_x ; after the transition its kinetic energy is $\epsilon(k_x - w_x)$, as the particle loses ϵw_x in moving uphill. We call $\epsilon(k_x - w_x)$ the spare kinetic energy of the transition. If there is a particle at $x + \ell$ and a hole at x , the particle can move down to x whatever its kinetic energy happens to be. This move is the inverse to the first, and to arrive at a symmetric Markov matrix, we choose the transition rates for these two processes to be the same. We have argued [23] that a good model for the transition matrix is to choose the rate to be proportional to the spare kinetic energy, by analogy with Einstein’s hypothesis of stimulated emission. To this, we add one more unit (the ‘spontaneous emission’) which in the event makes no difference to the continuum limit.

We see from our answer, eq. (2), that this choice leads to a linear increase in the thermal conductivity with temperature, roughly in accord with experiments [14], p. 574, for various gases in the range $100^\circ - 300^\circ K$. It also leads to a diffusion rate that increases linearly, [23], as chosen by Smoluchowski.

Let $x \in \Lambda$; let ω and ω' be two sample points on the same $\Omega_{E,n}$, and let $\omega'_y = \omega_y$ for $y \neq x$ or $x + \ell$. Suppose that $\omega_x = k_x \geq w_x$, and $\omega_{x+\ell} = \emptyset$, $\omega'_x = \emptyset$ and $\omega'_{x+\ell} = k_x - w_x$. We call this the hopping criterion, and define the transition matrix T_x by

$$T_x = \begin{array}{cc} \omega & \omega' \\ \omega & 1 - 2\lambda\epsilon(k_x - w_x + 1) \quad 2\lambda\epsilon(k_x - w_x + 1) \\ \omega' & 2\lambda\epsilon(k_x - w_x + 1) \quad 1 - 2\lambda\epsilon(k_x - w_x + 1) \end{array} \quad (16)$$

It was noticed in [23, 24] that transition rates which grow with energy need care when the time is discrete, as the transition probability becomes larger than 1 for large energies; the stay-as-you-were probability can become negative. Not only is this unphysical; it leads to unstable difference equations and spurious chaos [18]. It is therefore desirable in our model to cut off the hopping probability to zero above

$$k_{\max} = (2\lambda\epsilon)^{-1} - 1. \quad (17)$$

By making ϵ smaller we can make this cut-off as large as we please. For simplicity of notation, we put the matrix elements of T_x equal to zero unless ω and ω' obey the hopping criterion. That is, we remove the diagonal line of units. A matrix like T_x can be defined for each $x \in \Lambda$. In particular, $T_{x-\ell}$ describes the move down from x to $x - \ell$, and the move up from $x - \ell$ to x , which is assigned the probability

$$2\lambda\epsilon(k_{x-\ell} - w_{x-\ell} + 1) = 2\lambda\epsilon(k_x + 1), \quad (18)$$

or zero if $k_{x-\ell} < w_{x-\ell}$.

Both T_x and $T_{x-\ell}$ affect the population at x , but other transitions, T_y , $y \neq x, x - \ell$, do not. We define the linear part of the local dynamics at x to be $(T_x + T_{x-\ell})/2$, and the full linear dynamics to be given by the symmetric Markov matrix

$$T = \sum_x (T_x + T_{x-\ell})/2. \quad (19)$$

The next step in statistical dynamics, the analogue of the Stosszahlansatz, is the specification of the thermalising map Q . This projects the result of one time-step, $p \mapsto Tp$, onto a subset of states called the information manifold. We seek to implement mathematically the physical idea that the kinetic energy at a point x completely thermalises in one time step. The description of the local state by the full distribution of the random variable \mathcal{K}_x is replaced by one variable, the temperature $\Theta(x)$. According to [15, 1] we have to choose a subspace \mathcal{X} of slow variables, spanned by $\{X_0 = 1, X_1 = H, X_2, \dots, X_N\}$, in the notation of [20]. Given a state p , we record the mean values

$$\eta_j = p.X_j, \quad j = 1, 2, \dots, N; \quad (20)$$

we then define Qp to be the state of maximum entropy having these mean values. The set of states $\mathcal{M}(\mathcal{X}) = \{Qp : p \in \Sigma\}$ has a Riemannian structure,

and is called the *information manifold* of \mathcal{X} . It is parametrised by the means, which are called the mixture coordinates. If we start with $p \in \mathcal{M}$, we define one time-step of the full (non-linear) dynamics to be $p \mapsto QTp$. This maps \mathcal{M} to itself, and is given by difference equations in N variables. This is far fewer than needed for the linear dynamics.

In the present model, we take the slow variables to be the span of $\{\mathcal{N}_x : x \in \Lambda\} \cup \{\mathcal{K}_x : x \in \Lambda\}$, a total of $N = 2|\Lambda|$ variables. In particular the total energy is a slow variable. Let us denote the means of \mathcal{N}_x and \mathcal{K}_x by the fields n_x and K_x :

$$n_x = p \cdot \mathcal{N}_x; \quad K_x = p \cdot \mathcal{K}_x. \quad (21)$$

The algebra of observables, \mathcal{A} , is the tensor product

$$\mathcal{A} = \otimes_x \mathcal{A}_x \quad (22)$$

of local algebras. The state Qp is then the state of maximum entropy with these means; it is well known that this is the state in *LTE*, the product of local grand canonical states, independent over Λ ; thus

$$Qp(\omega) = \prod_x p_x(\omega_x) \quad (23)$$

where p_x is the marginal probability of p on Ω_x . In its turn, p_x is the state on Ω_x of maximum entropy among states with given means n_x, K_x . It is therefore the (fermionic) grand canonical state, and so has the form, for some parameter β_x :

$$p_x(\emptyset) = 1 - n_x \quad (24)$$

$$p_x(k) = n_x Z_x^{-1} e^{-\epsilon k \beta_x}, \quad (25)$$

where $Z_x = (1 - \exp(-\epsilon \beta_x))^{-1}$. We determine β_x or the temperature $\Theta_x = 1/(k_B \beta_x)$, from the mean-value K_x :

$$K(x) = p \cdot \mathcal{K}_x = \epsilon n_x \sum_{k=0} k Z_x^{-1} e^{-\epsilon k \beta_x} \quad (26)$$

$$= \frac{\epsilon n_x}{e^{\epsilon \beta_x} - 1}. \quad (27)$$

Here we have taken the sums up to infinity, neglecting the term $\exp(-\beta k_{\max} \epsilon)$ compared to 1.

We note that

$$n(x) = \sum_{k \geq 0} p_x(k) \quad (28)$$

$$e^{-\epsilon\beta} = (1 + \epsilon n/K)^{-1} \quad (29)$$

$$Z = 1 + K/(\epsilon n). \quad (30)$$

Our strategy for specifying one time-step in the dynamics is to start with $p \in \mathcal{M}$, and so of the form eq. (23), (25), (30), and then find $\hat{p} = Tp$, or rather, its marginals. From the marginals of \hat{p} we find the new values $\hat{n}(x)$, $\hat{K}(x)$ of the mixture coordinates; from these we can find the new $\exp(\epsilon\hat{\beta}) = 1 + \epsilon\hat{n}/\hat{K}$. It remains to explain how to find the marginals of \hat{p} .

For a product state over Λ , eq. (23), the probability of the set of points like ω , satisfying the hopping criteria at x , (i.e. x occupied with kinetic energy ϵk_x , and $x+\ell$ empty) is $p(x, k)(1 - n_{x+\ell})$. Similarly, the set of points like ω' , (i.e. with x empty, and $x+\ell$ occupied with kinetic energy $\epsilon(k_x - w_x)$) is $p(x + \ell, k_x - w_x)(1 - n_x)$. The other sites $y \neq x, x + \ell$ are unaffected by T_x and these factors in eq. (23) can be summed over ω_y to give unity. Thus the marginal at x of $T_x p$ is

$$\begin{aligned} T_x p(x, k) &= p(x, k) - p(x, k) (1 - n_{x-\ell}) 2\lambda\epsilon (k + 1 - w_x) \\ &+ p(x + \ell, k - w_x) (1 - n_x) 2\lambda\epsilon (k + 1 - w_x). \end{aligned} \quad (31)$$

Similarly

$$\begin{aligned} T_{x-\ell} p(x, k) &= p(x, k) - p(x, k) (1 - n_{x-\ell}) 2\lambda\epsilon (k_{x-\ell} - w_{x-\ell} + 1) \\ &+ p(x - \ell, k_{x-\ell}) (1 - n_x) 2\lambda (k_{x-\ell} - w_{x-\ell} + 1). \end{aligned} \quad (32)$$

Here, $k = k_{x-\ell} - w_{x-\ell}$ must hold, to conserve energy in the transition. So the change in the marginal at x due to $(T_x + T_{x-\ell})/2$, and therefore to T , simplifies a bit to

$$\begin{aligned} \hat{p}(x, k) &= p(x, k) - p(x, k) (1 - n_{x-\ell}) \lambda\epsilon (k + 1 - w_x) \\ &+ p(x + \ell, k - w_x) (1 - n_x) \lambda\epsilon (k + 1 - w_x) \\ &- p(x, k) (1 - n_{x-\ell}) \lambda\epsilon (k + 1) \\ &+ p(x - \ell, k + w_{x-\ell}) (1 - n_x) \lambda\epsilon (k + 1). \end{aligned} \quad (33)$$

From this we can find the new values, the one-step updates, \hat{n} , \hat{K} :

$$\hat{n}_x = \sum_{k \geq 0} \hat{p}(x, k)$$

$$\begin{aligned}
&= n_x - \lambda \epsilon n_x (1 - n_{x+\ell}) Z_x^{-1} \sum_{k \geq w_x} (k+1 - w_x) e^{-\epsilon k \beta_x} \\
&+ \lambda \epsilon n_{x+\ell} (1 - n_x) Z_{x+\ell}^{-1} \sum_{k \geq w_x} (k+1 - w_x) e^{-\epsilon(k-w_x)\beta_{x+\ell}} \\
&- \lambda \epsilon n_x (1 - n_{x-\ell}) Z_x^{-1} \sum_{k \geq 0} (k+1) e^{-\epsilon k \beta_x} \\
&+ \lambda \epsilon n_{x-\ell} (1 - n_x) Z_{x-\ell}^{-1} \sum_{k \geq 0} (k+1) e^{-\epsilon(k+w_{x-\ell})\beta_{x-\ell}}, \tag{34}
\end{aligned}$$

and

$$\begin{aligned}
\hat{K}_x &= \sum_{k \geq 0} \epsilon k \hat{p}(x, k) \\
&= K_x - \epsilon^2 \lambda n_x (1 - n_{x+\ell}) Z_x^{-1} \sum_{k \geq w_x} k (k+1 - w_x) e^{-\epsilon k \beta_x} \\
&+ \epsilon^2 \lambda n_{x+\ell} (1 - n_x) Z_{x+\ell}^{-1} \sum_{k \geq w_x} k (k+1 - w_x) e^{-\epsilon(k-w_x)\beta_{x+\ell}} \\
&- \epsilon^2 \lambda n_x (1 - n_{x-\ell}) Z_x^{-1} \sum_{k \geq 0} k (k+1) e^{-\epsilon k \beta_x} \\
&+ \epsilon^2 \lambda n_{x-\ell} (1 - n_x) Z_{x-\ell}^{-1} \sum_{k \geq 0} k (k+1) e^{-\epsilon(k+w_{x-\ell})\beta_{x-\ell}}. \tag{35}
\end{aligned}$$

The sum should go up to the largest k consistent with the positivity of the diagonal matrix element of $T_{\omega, \omega'}$ at x and $x-\ell$. This ensures that the model is entropy increasing, and that the discrete dynamics is stable.

The dynamics is the explicit map $n \mapsto \hat{n}$, $K \mapsto \hat{K}$, and from \hat{K} we can compute $\hat{\beta}$, and thus get the new point of \mathcal{M} . In the next section we take the continuum limit of this dynamics. The numerical solution of the resulting reaction-diffusion equations might be best done using these discrete equations: energy is conserved and entropy increases in all approximations, which ensures that the numerical solutions have reasonable physical properties, and do not exhibit spurious chaos, (chaos not present in the continuum equations).

3 The Continuum Limit

We now take the continuum limit of the updating equations, thus:

$$dt = \ell^2 \rightarrow 0; \quad \epsilon = \gamma \ell \rightarrow 0 \quad (\gamma \text{ fixed}) \tag{36}$$

$$\frac{\hat{K} - K}{dt} \rightarrow \frac{\partial K}{\partial t}; \quad \frac{1}{\ell} \rightarrow \rho_m; \quad \rho = \frac{n}{\ell} \quad (37)$$

$$\frac{V(x + \ell) - V(x)}{\ell} \rightarrow \frac{\partial V}{\partial x} \quad \text{and so on.} \quad (38)$$

This is achieved by writing

$$\beta_{x \pm \ell} = \beta \pm \ell \beta_1 + (1/2)\ell^2 \beta_2 \quad (39)$$

$$n_{x \pm \ell} = n \pm \ell n_1 + (1/2)\ell^2 n_2 \quad (40)$$

$$\epsilon w_{x - \ell} = V(x) - V(x - \ell) = \ell V_1 - (1/2)\ell^2 V_2 \quad (41)$$

$$\hat{n} - n = A_1 + A_2 + A_3 + A_4. \quad (42)$$

Here, β_1 is first the derivative of β , β_2 is the second derivative, and the same for the functions n and V ; the A's are four expressions in eq. (34):

$$A_1 = -\epsilon \lambda n(1 - n_3) e^{-\epsilon w \beta} \left(1 - e^{-\epsilon \beta}\right) \sum_{k \geq 0} (k + 1) e^{-\epsilon \beta k} \quad (43)$$

$$A_2 = \epsilon \lambda n_3(1 - n) \left(1 - e^{-\epsilon \beta_3}\right) \sum_{k \geq 0} (k + 1) e^{-\epsilon \beta_3 k} \quad (44)$$

$$A_3 = -\epsilon \lambda n(1 - n_4) \left(1 - e^{-\epsilon \beta}\right) \sum_{k \geq 0} (k + 1) e^{-\epsilon \beta k} \quad (45)$$

$$A_4 = \epsilon \lambda n_4(1 - n) \left(1 - e^{-\epsilon \beta_4}\right) e^{-\epsilon \beta_4 w_4} \sum_{k \geq 0} (k + 1) e^{-\epsilon \beta_4 k}, \quad (46)$$

where $\beta_3 = \beta_{x + \ell}$, $\beta_4 = \beta_{x - \ell}$, $n_3 = n_{x + \ell}$, $n_4 = n_{x - \ell}$, $w_4 = w_{x - \ell}$. The sum is allowed to go to infinity in the continuum limit.

We ask MAPLE to evaluate $\hat{n} - n$ to lowest non-vanishing order in ℓ , namely, ℓ^2 ; we substitute $\epsilon = \gamma \ell$, with γ fixed, $n_3 = n + \ell n' + (1/2)\ell^2 n''$ etc., $\beta(x) = 1/\Theta(x)$, and $\hat{n} - n$ by $\ell^2 \partial n / \partial t$. In one dimension the result, as $\ell \rightarrow 0$, is

$$\frac{\partial n}{\partial t} + \text{div } j_n = 0 \quad (47)$$

where

$$j_n = -\lambda (\Theta n' + (\Theta' + V') n(1 - n)). \quad (48)$$

We see that this is independent of γ .

The particle density is $n/\ell = \rho$; then $n = \rho \ell$ which we replace by ρ/ρ_m rather than by zero in the limit. So by dividing eq. (48) by ℓ gives our equation of motion for the particle density:

$$j_c = -\lambda (\Theta \nabla \rho + \rho(1 - \rho/\rho_m) \nabla (\Theta + V)). \quad (49)$$

The term $\lambda\rho(1-\rho/\rho_m)\nabla\Theta$ is the thermal diffusion; if $\rho \ll \rho_m$ we see that the Soret coefficient is exactly λ , but that for dense fluids (near solidification) it is smaller. The Soret term is absent in the model of dense fluids presented in [22]. This arises because there the particles do not carry heat, unlike those of the present model.

For the kinetic energy density $K(x)$, we write

$$\hat{K} - K = A1 + A2 + A3 + A4, \quad (50)$$

where

$$A1 = -\epsilon^2 \lambda n(1-n3) \left(1 - e^{-\epsilon\beta}\right) e^{-\epsilon\beta w} \sum_{k \geq 0} (k+w)(k+1) e^{-\epsilon\beta k} \quad (51)$$

$$A2 = \epsilon^2 \lambda(1-n)n3 \left(1 - e^{-\epsilon\beta 3}\right) \sum_{k \geq 0} (k+w)(k+1) e^{-\epsilon\beta 3k} \quad (52)$$

$$A3 = -\epsilon^2 \lambda n(1-n4) \left(1 - e^{-\epsilon\beta}\right) \sum_{k \geq 0} k(k+1) e^{-\epsilon\beta k} \quad (53)$$

$$A4 = \epsilon^2 \lambda n4(1-n) \left(1 - e^{-\epsilon\beta 4}\right) e^{-\epsilon\beta 4 w} \sum_{k \geq 0} k(k+1) e^{-\epsilon\beta 4k}. \quad (54)$$

Now we put $K = n\Theta$ and take the limit $\ell \rightarrow 0$; MAPLE gives

$$\begin{aligned} \frac{\partial(n\Theta)}{\partial t} &= -\lambda \left\{ n^2(V')^2 - 3V'n'\Theta - 3V'n\Theta' - n(V')^2 \right. \\ &\quad + 4n^2(\Theta')^2 + 4n^2\Theta\Theta'' - 4n\Theta\Theta'' + 2n^2\Theta V'' \\ &\quad + 3n^2V'\Theta' + 8n\Theta\Theta'n' + 4nn'V'\Theta \\ &\quad \left. - 2n''\Theta^2 - 8n'\Theta\Theta' - 2n\Theta V'' - 4n(\Theta')^2 \right\} \\ &= -j_n V' - 2\text{div}(\Theta j_n) + 2\lambda \text{div}(\Theta(1-n)n\Theta'). \end{aligned} \quad (55)$$

Again we see that γ drops out. Putting $n/\ell = \rho$ and $1/\ell = \rho_m$ we get in ν -dimensions:

$$\frac{\partial(\rho\Theta)}{\partial t} = -j_c \cdot \nabla V - 2\text{div}(\Theta j_c) + 2\lambda \text{div}(\Theta\rho(1-\rho/\rho_m)\nabla\Theta). \quad (56)$$

Thus, at least at a formal level, the equations discussed in §1 are ‘derived’ from a discrete stochastic model. Our derivation has not proved that the solutions to the discrete equations converge to solutions of the nonlinear coupled equations in the continuum. Indeed these are not uniformly elliptic, and a proof of existence of even local solutions needs care. Some results for similar systems are presented in [25, 2, 3].

4 The Onsager Form

We now argue that only the ‘anomalous’ part of the Dufour effect is the true Onsager dual to the Soret effect. We see this in the model of [22]; this model has no Soret effect, but the heat current does contain the normal convection term Θj_c . In the classical Boltzmann equation the heat content of a fluid is $3/2\Theta\rho$, instead of our $\Theta\rho$; we would expect, then, a convection term $3/2\Theta j_c$ in the heat current. However, in [6] the term $5/2\Theta j_c$ is found. We see that of this, $3/2\Theta j_c$ is normal convection, and Θj_c is anomalous convection; the latter is the same as in the present model. We shall show that Onsager symmetry relates the Soret effect to the anomalous part of the convection.

Both the model of [22], and the present model, have the same sample space, slow variables and conserved quantities, namely the particle number and energy. It follows from the argument given in [23] that both models have the same entropy and thermodynamic forces. They differ in their dynamics, which in Onsager theory is determined by the way the currents depend on the forces. We first find the entropy of the discrete model, and then take its formal continuum limit. The entropy of the state

$$p(\omega) = \prod_x \{(1 - \mathcal{N}_x(\omega))(1 - n_x) + \mathcal{N}_x(\omega)p_x(\omega_x)\} \quad (57)$$

which is independent over Λ , is the sum of the contributions at each x ; thus

$$\begin{aligned} S(p) &= - \sum_{\omega} p(\omega) \log p(\omega) \\ &= - \sum_x (1 - n_x) \log (1 - n_x) - \sum_x n_x \sum_{k \geq 0} p_x(k) \log p_x(k) \\ &= - \sum_x (1 - n_x) \log (1 - n_x) - \sum_x n_x \log n_x \\ &\quad + \sum_x n_x \left\{ \log Z_{\beta_x} + \beta_x \epsilon / \left(e^{\epsilon \beta_x} - 1 \right) \right\} \end{aligned} \quad (58)$$

Now,

$$- \sum_x n_x \log n_x = - \sum_x (1 - n_x) \log (1 - n_x) \quad (59)$$

$$= - \sum_x \frac{n_x}{\ell} \left(\log \frac{n_x}{\ell} + \log \ell \right) \ell = - \sum_x \left(\frac{1}{\ell} - \frac{n_x}{\ell} \right) \log (1 - n_x) \quad (60)$$

and in the continuum limit, $\ell \rightarrow 0$, $\sum_x \ell$ becomes $\int dx$, n_x/ℓ becomes $\rho(x)$ and $1/\ell$ becomes ρ_m . So the dichotomic part of the entropy becomes the

differential entropy

$$- \int \rho(x) \log \rho(x) dx - \int (\rho_m - \rho) \log (1 - \rho/\rho_m) dx, \quad (61)$$

apart from the large positive term

$$- \log \ell \int \rho(x) dx. \quad (62)$$

However, this term can be dropped; for $\int \rho(x) dx$ is constant in time, so the divergent term does not contribute to dS/dt . The Gibbsian term in S_x also has a simple limit:

$$\begin{aligned} n_x (\log Z_{\beta_x} + \beta_x K_x) &= n_x \left(-\log (1 - e^{-\epsilon \beta_x}) + \beta_x \epsilon / (e^{\epsilon \beta} - 1) \right) \\ &= -n_x \log \epsilon - n_x \log \beta_x + n_x + O(\epsilon). \end{aligned} \quad (63)$$

Again, summing over x leads to the divergent but constant terms $(-\log \epsilon + 1) \sum_x n_x$, which can be dropped, leaving

$$- \sum_x \log \beta_x n_x \rightarrow \int \rho(x) \log \Theta(x) dx;$$

The continuum entropy is therefore

$$\begin{aligned} S &= - \int \rho(x) \log \rho(x) dx - \int (\rho_m - \rho) \log (1 - \rho/\rho_m) dx \\ &\quad + \int \rho \log \Theta(x) dx, \end{aligned}$$

as claimed in [22], eq. (49).

The next step [23] in setting up a comparison with Onsager theory is to write \dot{S} as a (continuous version) of Onsager's ansatz [10]

$$\Theta \dot{S} = \sum_{\alpha} X^{\alpha} j_{\alpha}. \quad (64)$$

We use the identities

$$\int \rho \dot{\Theta} / \Theta dx = \int (\rho \dot{\Theta}) / \Theta dx \quad (65)$$

$$\int \rho \dot{\rho} / \rho dx = \int (\rho_m - \rho) \dot{\rho} / (\rho_m (\rho_m - \rho)) dx = 0 \quad (66)$$

to get

$$\begin{aligned}\dot{S} &= - \int \dot{\rho} \log \rho \, dx + \int \dot{\rho} \log (1 - \rho/\rho_m) \, dx \\ &+ \int \dot{\rho} \log \Theta \, dx + \int (\rho \dot{\Theta})/\Theta \, dx.\end{aligned}\quad (67)$$

In both the present model and that of [22] there are two conserved densities, the particle number ρ and the energy $\mathcal{E} = \rho(V + \Theta)$; thus $\rho \dot{\Theta} = \dot{\mathcal{E}} - \dot{\rho}V$. We impose the condition of ‘no flow’ on the boundary, $\partial\Lambda$, which could be at infinity. Thus the components of the current normal to the boundary, j_c^\perp and j_e^\perp , vanish on $\partial\Lambda$. In both models, then, we use the conservation laws and then integrate by parts in eq. (67) and discard the boundary term, to get:

$$\begin{aligned}\dot{S} &= - \int \dot{\rho} (\log(\rho\rho_m/(\rho_m - \rho)) - \log \Theta) + \int (\dot{\mathcal{E}} - \dot{\rho}V)/\Theta \, dx \quad (68) \\ &= - \int j_c \cdot \nabla (\log(\rho/(1 - \rho/\rho_m)) - \log \Theta + V/\Theta) \, dx \\ &+ \int j_e \cdot \nabla (1/\Theta) \, dx.\end{aligned}\quad (69)$$

This is true whatever the equation of motion, provided that the particle number and energy are conserved. In particular, we can vary the hopping probability, λ , as a function of (x, t) , so that j_c and j_e are arbitrary functions. So from the Onsager ansatz for \dot{S} we can read off the thermodynamic forces

$$\frac{X^c}{\Theta} = -\nabla \left\{ \log \left(\frac{\rho}{1 - \rho/\rho_m} \right) + \frac{V}{\Theta} - \log \Theta \right\} \quad (70)$$

$$= -\frac{1}{\rho(1 - \rho/\rho_m)} \left\{ \nabla \rho + \frac{\nabla V}{\Theta} \rho(1 - \rho/\rho_m) \right\} - (V + \Theta) \nabla \left(\frac{1}{\Theta} \right); \quad (71)$$

$$\frac{X^e}{\Theta} = \nabla \frac{1}{\Theta}. \quad (72)$$

These expressions for the thermodynamic forces conjugate to the currents j_c and j_e hold for both models; we consider them in turn. In the model of [22] the equations of motion are

$$j_c = -\lambda \left\{ \nabla \rho + \rho(1 - \rho/\rho_m) \frac{\nabla V}{\Theta} \right\} \quad (73)$$

$$j_e = -\lambda \{ \rho(1 - \rho/\rho_m) \nabla \Theta \} + (\Theta + V) j_c. \quad (74)$$

This model has no Soret effect, but shows the ‘normal’ convection, in our terminology, because of the contribution Θj_c to the heat current. This will be observed as the Dufour effect, since there is a heat flow if $\nabla\Theta = 0$ but $\nabla\rho \neq 0$. Somewhat luckily (for Onsager theory), the currents are linear expressions in X^c and X^e , with no derivatives, but with nonlinear coefficients:

$$j_c = \lambda\rho(1 - \rho/\rho_m) \frac{X^c}{\Theta} + \lambda(V + \Theta)\rho(1 - \rho/\rho_m) \frac{X^e}{\Theta}; \quad (75)$$

$$j_e = (V + \Theta)\lambda\rho(1 - \rho/\rho_m) \frac{X^c}{\Theta} + \lambda\left\{\lambda\rho(1 - \rho/\rho_m)\Theta^2 + (\Theta + V)^2\rho(1 - \rho/\rho_m)\right\} \frac{X^e}{\Theta}. \quad (76)$$

We see that Onsager symmetry holds, and that the Onsager matrix is positive definite. Hence entropy is an increasing function of time, as expected.

In the present model, we see that the currents, given in eq. (2), can be expressed in terms of the *same* thermodynamic forces eq. (72) thus:

$$j_c = \lambda\rho(1 - \rho/\rho_m) \frac{X^c}{\Theta} + \lambda(V + 2\Theta)\rho(1 - \rho/\rho_m) \frac{X^e}{\Theta} \quad (77)$$

$$j_e = (V + 2\Theta)\lambda\rho(1 - \rho/\rho_m) \frac{X^c}{\Theta} + \lambda\left\{(V + 2\Theta)^2\rho(1 - \rho/\rho_m) + 2\Theta^3\rho(1 - \rho/\rho_m)\right\} \frac{X^e}{\Theta}. \quad (78)$$

Again, Onsager symmetry and positivity hold. The anomalous part of the convection, the factor ‘2’ in $V + 2\Theta$, can be inferred using Onsager symmetry and the Soret term, $\nabla\Theta$, in j_c . In our approach, all these properties, the Soret effect, the anomalous Dufour effect and the Onsager symmetry, follow from the model, rather than being put in, as in the Onsager theory.

We can relate the thermodynamic forces to the gradients of the canonical coordinates $\xi^\alpha(x)$ of the information manifold (when the states are independent over Λ), according to the general theory; see eq. (15) of [23]. We shall now verify that this is true in this model, in the continuum limit. Recall that in the discrete model we write the density matrix as

$$\rho = e^{-\sum_0 \xi^\alpha H_\alpha}. \quad (79)$$

Here, $H_0 = 1$, $\xi^0 = \log \Xi$, where Ξ is the grand partition function; the H_α are the conserved densities. In our model, these are the number of particles

at x , \mathcal{N}_x , and the energy at x , $\mathcal{E}_x = \mathcal{V}_x + \mathcal{K}_x$. A point on the information manifold, for finite Λ , is the product over x of a probability which we write in the usual form of a local equilibrium state:

$$p(x) = e^{-\log \Xi} e^{-\beta_x(\mathcal{E}_x - \mu_x \mathcal{N}_x)}. \quad (80)$$

We can thus identify the canonical coordinates as $\xi_x^c = -\beta_x \mu_x$ and, as expected, $\xi_x^e = \beta_x$. To relate ξ^c to n , one of the mixture coordinates, note that (omitting the label x)

$$\Xi^{-1} = 1 - n \quad (81)$$

and

$$\Xi = \sum_{\omega} e^{\beta \mu \mathcal{N}} e^{-\beta \mathcal{E}} \quad (82)$$

$$\begin{aligned} &= 1 + e^{\beta(\mu - V)} \sum_{k \geq 0} e^{-\epsilon \beta k} \\ &= 1 + \frac{e^{\beta(\mu - V)}}{1 - e^{-\epsilon \beta}}. \end{aligned} \quad (83)$$

We combine eq. (81) with eq. (83) to get

$$\beta \mu = \beta V + \log(n/(1 - n)) + \log(1 - e^{-\epsilon \beta}) \quad (84)$$

$$= \beta V + \log \frac{\rho}{\rho - \rho/\rho_m} + \log \epsilon - \log \beta + O(\epsilon) \quad (85)$$

for small ϵ . In the continuum limit we drop the infinite constant $\log \epsilon$, as only the gradient is used. Thus we get

$$\xi^c = -\beta \mu = -\log \frac{\rho}{1 - \rho/\rho_m} + \log \Theta - \frac{V}{\Theta} \quad (86)$$

and $X^c/\Theta = \nabla \xi^c$, using eq. (70). This, together with eq. (72) shows that (ξ^e, ξ^c) are “potentials” for $(-X^e/\Theta, -X^c/\Theta)$.

5 Conclusion

We have constructed an example of nonequilibrium thermodynamics obeying the first and second laws, and which exhibits the Soret and Dufour effects. Apart from the hard core, no interparticle potential is postulated, and indeed the effects persist in the limit $\rho_m \rightarrow \infty$, corresponding to no

hard core. This should be compared with the kinetic theory described in [6], p.103; this gives the impression that the Soret and Dufour effects depend on the careful inclusion of interparticle forces and that they are present only in gas mixtures. In our approach the effect of the interparticle forces are included only indirectly, in that the dynamics includes the thermalising map Q , which ensures that the motion is confined to the information manifold. Thus, whatever the forces are, they keep the system in local thermodynamic equilibrium. This leads to a simple understanding of the effects; regions of higher temperature contain more high-speed molecules than regions of low temperature, and so they preferentially move from high to low temperatures. In our model there is no velocity variable, and by high speed we mean molecules that hop with greater probability. In [6] an abnormal convection is also found, and is interpreted as “convection of enthalpy”. It is the differential Soret effect between isotopes that is emphasised there. This is the reason for the great industrial importance of the effect; it allows gas mixtures to be separated by a heat gradient. To get this effect we would need to allow the hopping rate λ to depend on the mass of the molecule.

We have remarked that the density of states in our model is unity; in a semiclassical model in one dimension, there are two states of each energy, corresponding to the two directions of motion, so apart from this trivial factor, it would appear that our model is one dimensional. However, the hopping rate is not that of a particle in one dimension. In the free dynamics between collisions the rate of movement is proportional to the velocity i.e. $E^{1/2}$, whereas in our model it is proportional to the spare kinetic energy E . This larger hopping rate partially compensates for the lack of multiplicity of states, as can be seen by the following argument. In three dimensions the number of states of a single particle in the semiclassical model is proportional to the volume of phase space, and thus has a factor $p^2 dp$ (where p is now the momentum) which is proportional to $E^{1/2} dE$. Suppose a particle in three dimensions at a lattice site $x \in \Lambda$ having momentum p hops to a neighbouring site, $x + \ell$ against the force given by the gradient of the potential V . Its momentum after the transition will be slightly different, say p' , which is determined by p and the force. Thus each of the many states at x can make a momentum-conserving transition to only one of the many states of the right energy at $x + \ell$. So the number of states making the transition is proportional to the number of states, namely $E^{1/2}$. The rate of flow of such an element of phase space is proportional to $E^{1/2}$ as well, so the number making the transition is $En(E)$, where $n(E)$ is the occupation number. This is the same as that due to stimulated hopping, as assumed in the present

paper in eq. (18). As we saw, the extra hop due to spontaneous hopping did not contribute to the continuum limit. It should be mentioned that this does not mean that model of the present paper gives the same answer (apart from trivial factors) as a three-dimensional model with the “correct” multiplicity, and rates proportional to the speed. Indeed, the factors Z^{-1} in the rate equations eq. (34) and (35) also depend on the multiplicity. These factors are proportional to $\Theta^{-3/2}$ instead of Θ^{-1} as in the present paper.

We can also regard the present model as describing a dense liquid of complex atoms, which have little kinetic energy, but which have a large number of excited states modelled by the levels ϵk , $k = 0, 1, 2, \dots, k_{\max}$. As remarked, to get the equations (1) and (2), we approximate $(1 - \exp(-\beta \epsilon k_{\max}))$ by 1, which requires that the temperature is low enough so that the states of high energy are not excited much. The density of states can be independently checked by experiment. For such a liquid, it would be interesting to see whether it is true that Dufour effect is double the convection (the factor 2 in eq. (2)).

Our model is more in the spirit of the discrete energy Boltzmann equations [16] than the discrete velocity models [17] which conserve momentum as well as energy. For example, [8] considers a lattice gas version of the Boltzmann equation, with a collision term between pairs of particles. The Dufour effect is predicted. In [8], only two speeds occur. The number of particles having each speed is separately conserved, so there is no thermal mixing in the scattering. The up-date equations for the densities are of the eighth degree. The authors compare numerical simulations of the exact model with solutions to a simplified model in which the momentum is put equal to zero, and a thermalising assumption is imposed. They remark that the simplified model is very close to the simulations. Our result shows that the Soret effect as well as the Dufour effect can be obtained without the two-body scattering.

We may rather easily vary the lattice shape, and allow hopping to next-nearest neighbours; we tried several such variants, and got the same continuum limit provided that we adjusted λ so that the finite-difference operator in the transition matrix T approximates the Laplacian. So the limit is rather robust.

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6 The Maple V Program

6.1 The Density

```
#We use the notation  $n1 = dn/dx$ ,  $n2 = d^2n/dx^2$ ,  
#  $n3=n(x+1)$ ,  $n4=n(x-1)$ , and the same for  
#  $\beta$  and  $w$ .  
assume(epsilon>0);assume(beta>0);  
A1:=-lambda*epsilon*n*(1-n3)*exp(-epsilon*beta*w)*(1-exp(-epsilon*beta))*  
sum((k+1)*exp(-epsilon*beta*k),k=0..infinity);  
B1:=simplify(A1);  
C1:=series(B1,epsilon,5);  
D1:=convert(C1,polynomial);  
F1:=simplify(D1);  
G1:=subs(epsilon=l*gamma,F1);  
H1:=subs(n3=n+l*n1+(1/2)*l^2*n2,G1);  
J1:=series(H1,l,3);  
Z1:=convert(J1,polynomial);  
assume(beta3>0);  
A2:=epsilon*lambda*n3*(1-n)*(1-exp(-beta3*epsilon))*sum((k+1)*  
exp(-beta3*epsilon*k),k=0..infinity);  
B2:=series(A2,epsilon,5);  
C2:=convert(B2,polynomial);  
D2:=simplify(C2);  
F2:=subs(epsilon=l*gamma,D2);  
G2:=subs(n3=n+l*n1+(1/2)*l^2*n2,F2);  
H2:=subs(beta3=beta+l*beta1+(1/2)*l^2*beta2,G2);  
J2:=series(H2,l,3);  
K2:=convert(J2,polynomial);  
Z2:=simplify(K2);  
A3:=-epsilon*lambda*n*(1-n4)*(1-exp(-beta*epsilon))*sum((k+1)*  
exp(-beta*epsilon*k),k=0..infinity);  
B3:=series(A3,epsilon,5);  
C3:=convert(B3,polynomial);  
D3:=subs(epsilon=l*gamma,C3);  
F3:=subs(n4=n-l*n1+(1/2)*l^2*n2,D3);  
G3:=series(F3,l,3);  
H3:=convert(G3,polynomial);  
Z3:=simplify(H3);
```

```

assume(beta4>0);
A4:=epsilon*lambda*n4*(1-n)*(1-exp(-beta4*epsilon))*
exp(-beta4*epsilon*w4)*sum((k+1)*exp(-beta4*epsilon*k),k=0..infinity);
B4:=series(A4,epsilon,5);
C4:=convert(B4,polynom);
D4:=subs(epsilon=gamma*l,C4);
F4:=subs(n4=beta-l*n1+(1/2)*l^2*n2,D4);
G4:=subs(beta4=beta-l*beta1+(1/2)*l^2*beta2,F4);
H4:=subs(w4=w-l*w1+(1/2)*l^2*w2,G4);
J4:=series(H4,l,3);
K4:=convert(J4,polynom);
Z4:=simplify(K4);
ans1:=simplify(Z1+Z2+Z3+Z4);
ans2:=subs(beta=1/Theta(x),ans1);
ans3:=subs(beta1=diff(1/Theta(x),x),ans2);
ans4:=subs(beta2=diff(1/Theta(x),x$2),ans3);
ans5:=subs(w=diff(V(x),x),ans4);
ans6:=subs(w1=diff(V(x),x$2),ans5);
ans:=simplify(ans6);
Simple manipulation then gives eq. (1).

```

6.2 The Heat

```

‡ Soret2.ms; as before, we take the four terms from A to Z.
‡ beta1 denotes  $d\beta/dx$ , beta2 denotes  $d^2\beta/dx^2$ ,
‡ beta3 denotes  $\beta(x + \ell)$ ; beta4 denotes  $\beta(x - \ell)$ .
‡ and the same for n and w.
assume(beta>0); assume(epsilon>0);
A1:=-lambda*epsilon^2*n*(1-n3)*exp(-beta*epsilon*w)*
(1-exp(-beta*epsilon))*sum((k+w)*(k+1)*exp(-beta*epsilon*k),k=0..infinity);
B1:=simplify(A1);
C1:=series(B1,epsilon,6);
D1:=convert(C1,polynom);
F1:=subs(epsilon=l*gamma,D1);
G1:=subs(n3=n+l*n1+(1/2)*l^2*n2,F1);
H1:=series(G1,l,3);
J1:=convert(H1,polynom);
Z1:=simplify(J1);
assume(beta3>0);

```



```

A2:=epsilon^2*beta*(1-n)*n3*(1-exp(-epsilon*beta3))*sum((k+w)*(k+1)*exp(-
epsilon*beta3*k),k=0..infinity);
B2:=simplify(A2);
C2:=series(B2,epsilon,6);
D2:=convert(C2,polynom);
F2:=subs(epsilon=l*gamma,D2);
G2:=subs(n3=n+l*n1+(1/2)*1^2*n2,F2);
H2:=subs(beta3=beta+l*beta1+(1/2)*1^2*beta2,G2);
J2:=series(H2,l,3);
K2:=convert(J2,polynom);
Z2:=simplify(K2);
A3:=-epsilon^2*lambda*n*(1-n4)*(1-exp(-epsilon*beta))*sum(k*(k+1)*
exp(-epsilon*beta*k),k=0..infinity);
B3:=simplify(A3);
C3:=series(B3,epsilon,6);
D3:=convert(C3,polynom);
F3:=subs(epsilon=l*gamma,D3);
G3:=subs(n4=n-l*n1+(1/2)*1^2*n2);
H3:=series(G3,l,3);
K3:=convert(H3,polynom);
Z3:=simplify(K3);
assume(beta4>0);
A4:=epsilon^2*lambda*n4*(1-n)*(1-exp(-epsilon*beta4))*
exp(-epsilon*beta4*w4)*sum(k*(k+1)*exp(-epsilon*beta4*k),k=0..infinity);
B4:=simplify(A4);
C4:=series(B4,epsilon,6);
D4:=convert(C4,polynom);
F4:=subs(n4=n-l*n2+(1/2)*1^2*n2,D4);
G4:=subs(beta4=beta-l*beta1+(1/2)*1^2*beta2,F4);
H4:=subs(epsilon=l*gamma,G4);
J4:=subs(w4=w-l*w1+(1/2)*1^2*w2,H4);
K4:=series(J4,l,3);
L4:=convert(K4,polynom);
Z4:=simplify(L4);
ans1:=simplify(Z1+Z2+Z3+Z4);
ans2:=subs(w=V1/gamma,ans1);
ans3:=subs(w1=V2/gamma,ans2);
# Note that the result is of second degree in l and is independent
# of gamma.

```

```

ans4:=subs(beta=1/Theta(x),ans3);
ans5:=subs(beta1=diff(1/Theta(x),x),ans4);
ans6:=subs(beta2=diff(1/Theta(x),x$2),ans5);
Ans:=simplify(ans6);
This gives us eq. (55).

```